Comment on *Two-photon approximation in the theory of electron recombination in hydrogen* (D. Solovyev and L. Labzowsky, Phys. Rev. A 81, 062509 (2010)) *

S. G. Karshenboim†
Pulkovo Observatory, St.Petersburg, 196140, Russia and
Max-Planck-Institut für Quantenoptik, Garching, 85748, Germany

V. G. Ivanov
Pulkovo Observatory, St.Petersburg, 196140, Russia

J. Chluba
Canadian Institute for Theoretical Astrophysics, Toronto, ON M5S 3H8, Canada

The results for the total multi-photon decay rates of the $3p$ and $4s$ levels of hydrogen, presented by D. Solovyev and L. Labzowsky within the cascade approximation, are revisited. The corrected results for certain decay channels differ from original ones of those authors sometimes by order of magnitude. Some aspects with respect to the cosmological recombination process are clarified.

Paper [2] is devoted to the calculation of the contribution of various multi-photon decay modes to the lifetime of free hydrogenic energy levels. In particular, the multi-photon decays of the $3p$ and $4s$ state were considered.

Their result for the $3p$ radiative width, which includes three-photon decay modes (e.g. $3p \to 2s \to 1s$) within the cascade approximation, is given by Eq. (33) of [2]:

$$W^{\rm total}_{3p-1s} = W^{(1\gamma)}_{3p-1s} + \frac{3}{4}\,W^{(2\gamma)}_{3p-2p} + \frac{3}{4}\,\frac{W^{(1\gamma)}_{3p-2s}}{\Gamma_{3p}}\,W^{(2\gamma)}_{2s-1s}\ .$$

Here W_X is the probability of the related decay channel X, and Γ_A is the total radiative width (i.e. the total decay probability) of state A. Clearly, the radiative width, being calculated for a free atom, satisfies the condition

$$\Gamma_A = W^{\rm total}_{A-1s}\ ,$$

since any excited states should eventually decay into the ground state after emitting an appropriate number of photons.

Later on, equation (47) of [2] presents their result for the $4s$ radiative width, which includes four-photon modes (e.g., $4s \to 3p \to 2s \to 1s$) in the cascade approximation:

$$\begin{aligned} W^{\rm total}_{4s-1s} \ =\ & W^{(2\gamma)}_{4s-1s} + \frac{3}{2}\,\frac{W^{(1\gamma)}_{3s-2p}}{\Gamma_{3s}}\,W^{(2\gamma)}_{4s-3s} \\ & + \frac{3}{2}\,\frac{W^{(1\gamma)}_{4s-3p}}{\Gamma_{4s}}\,W^{(2\gamma)}_{3p-2p} \\ & + \frac{3}{2}\,\frac{W^{(1\gamma)}_{4s-3p}}{\Gamma_{4s}}\,\frac{W^{(1\gamma)}_{3p-2s}}{\Gamma_{3p}}\,W^{(2\gamma)}_{2s-1s}\ . \end{aligned}$$

Although expression (33) of [2] has the correct order of magnitude, i.e., $\propto \alpha(Z\alpha)^4 m_e c^2/\hbar$, we argue below that its numerical value is incorrect. Furthermore, the result given by Eq. (47) of [2] is even off by order of magnitude. The problem is that a conceptual mistake occurred in the calculation of the cascade terms involving three or four photons.

The appropriate results for $3p$ and $4s$ are well-known within the cascade approximation[1]. The results for all the decay channels, which contribute in order $\alpha(Z\alpha)^4 m_e c^2/\hbar$, are summarized in Table I (for the $3p$ state) and in Table II (for the $4s$ state).

Channel	Partial width	Partial width in [2]
$1\gamma: 3p \to 1s$	$W^{(1\gamma)}_{3p-1s}$	$W^{(1\gamma)}_{3p-1s}$
$3\gamma: 3p \to 2s \to 1s$	$W^{(1\gamma)}_{3p-2s}$	$\frac{3}{4}\,\frac{W^{(1\gamma)}_{3p-2s}}{\Gamma_{3p}}\,W^{(2\gamma)}_{2s-1s}$

TABLE I: The $3p$ decay channels and their partial width to order $\alpha(Z\alpha)^4 m_e c^2/\hbar$

Channel	Partial width	Partial width in [2]
$2\gamma: 4s \to 3p \to 1s$	$W^{(1\gamma)}_{4s-3p}\,\frac{W^{(1\gamma)}_{3p-1s}}{\Gamma_{3p}}$	not specified
$2\gamma: 4s \to 2p \to 1s$	$W^{(1\gamma)}_{4s-2p}$	not specified
$4\gamma: 4s \to 3p \to 2s \to 1s$	$W^{(1\gamma)}_{4s-3p}\,\frac{W^{(1\gamma)}_{3p-2s}}{\Gamma_{3p}}$	$\frac{3}{2}\,\frac{W^{(1\gamma)}_{4s-3p}}{\Gamma_{4s}}\,\frac{W^{(1\gamma)}_{3p-2s}}{\Gamma_{3p}}\,W^{(2\gamma)}_{2s-1s}$

TABLE II: The $4s$ decay channels and their partial width to order $\alpha(Z\alpha)^4 m_e c^2/\hbar$. The 2γ modes are not specified in more detail by the authors of [2]. However, a related comment in [2] indicates that some conceptual differences with our understanding of these channels exist (see below).

We note that the expressions Eqs. (29) and (38) of

---

*An extended version. A short version has been submitted to PRA [1].

†Electronic address: savely.karshenboim@mpq.mpg.de

[1] The cascade approximation for the dynamics of the decay implies a resonance approximation for the calculation of the related quantum-mechanical expressions. The description of various atomic-state decays resulting from the resonance approximation can be found in standard textbooks.

[2] introduce the total width of the $3p$ and $4s$ state, respectively. In the cascade approximation, which is sufficient for calculation of the leading order contributions and which is supposedly applied in [2], the width of any excited state (except for the $2s$ state) is the sum over $E1$ one-photon decays to all appropriate lower levels. This value is presented in various textbooks and summarized in the tables above. Apparently, once the state under question decays into lower-lying excited states, any further development due to a subsequent decay of those levels does not change the width of the initial state, a conceptual aspect that is different in the analysis of [2].

For the $3p$ state there are only two dominant channels, namely a 1γ decay ($3p \to 1s$) and a 3γ decay ($3p \to 2s \to 1s$). The probability of the second channel, which involves three photons, is indeed the same as a naive $E1$ 1γ probability of the $3p \to 2s$ decay, because for a free-atom case 100% of the atoms in the $2s$ state decay afterward into the $1s$ state with emission of two photons. All other channels and any corrections beyond the cascade approximation are of higher order in $(Z\alpha)$ and thus can be neglected. This implies that in particular the last term in Eq. (33) of [2] is incorrect, since it suggests that the total width of the $3p$ state is affected by the subsequent decay of the $2s$ state via two photons.

Technically, the difference originates from the regularization in Eq. (29) of [2]. Any cascade decay, calculated by means of Schrödinger's equation with a Hermitian quantum-mechanical Hamiltonian, leads to an expression with a denominator (or few denominators), value of which vanishes when the photon frequency is at resonance. The regularization should involve the non-zero width of the resonant intermediate state (states) as a regulator (regulators), as e.g. discussed in [3]. However, neither the width of the initial state (as is done in [2]) nor of the final state should be introduced. Once we substitute Γ_{2s} for Γ_{3p} in the denominator, the third term becomes of correct order. Still it has an incorrect coefficient of (3/4), which should be replaced by unity.

The second term in Eq. (33) describes the $3p \to 2p \to 1s$ channel and obviously its width should be equal to the width of the $3p \to 2p$ decay which appears in 2γ approximation and is of order $\alpha^2(Z\alpha)^6 m_e c^2/\hbar$. Apparently, the coefficient 3/4 in (33) is again incorrect and should be replaced by unity. However, although it is clear that a contribution of order $\alpha^2(Z\alpha)^6 m_e c^2/\hbar$ may be of interest for the differential probabilities of the decay process, it should be neglected in the total width, since many other corrections of this order (or even some larger contributions) are not accounted for (see [3, 4] for more detailed discussion).

In the case of the $4s$ state there are three basic modes. Two modes are for 2γ decay, namely, $4s \to np \to 1s$, ($n = 2, 3$), and one modes involve four photons ($4s \to 3p \to 2s \to 1s$). The probability of the $4s \to 2p \to 1s$ mode is the same as the $E1$ 1γ probability for the $4s \to 2p$, while the sum of decay widths for the two other channels, namely, of $4s \to 3p \to 1s$ and $4s \to 3p \to 2s \to 1s$, should reproduce the $E1$ 1γ width of $4s \to 3p$ decay, since the $3p$ state decays into $1s$ either directly or via the intermediate $2s$ level. The branching ratio for the $3p$ modes are

$$Br(3p - ns) = \frac{W^{(1\gamma)}_{3p-ns}}{W^{(1\gamma)}_{3p-1s} + W^{(1\gamma)}_{3p-2s}} \;,$$

where $n = 1, 2$. Since all the $2s$ states eventually decay into the ground state the probability of $3p \to 2s \to 1s$ decay is equal to the well-known probability of $3p \to 2s$ decay.

For the $4s$ state the leading 4γ term should read (see Table II)

$$W^{(1\gamma)}_{4s-3p} \frac{W^{(1\gamma)}_{3p-2s}}{\Gamma_{3p}} \;,$$

which is to be compared with the last term in Eq. (47) of [2]. The problem again comes from an incorrect regularization. Regularizing Eq. (38) properly, one can obtain the correct result after omitting the pre-factor 3/2 (which should be unity). This 4γ term is of the order of the $\alpha(Z\alpha)^4 m_e c^2/\hbar$.

The 2γ contributions (see Table II) are also of the same order of magnitude. The first term in Eq. (47) of [2] is intended to take these contributions into account, but is not specified any further by the authors of [2]. The correct 2γ result for the total $4s$ width should include cascade contributions, however, a comment after Eq. (48) of [2] refers to a numerical value of 12 s^{-1}, which seems more consistent[2] with a certain tail contribution beyond the cascade term obviously being of a higher order than $\alpha(Z\alpha)^4 m_e c^2/\hbar$.

The second and the third terms in Eq. (47) are of order $\alpha^2(Z\alpha)^6 m_e c^2/\hbar$ and, similar to our consideration of the $3p \to 2p$ channel, these terms may be in principle of interest for differential width, but should be neglected in the total width. Furthermore, the numerical coefficients 3/2 should be replaced with unity. In addition, for the third term the $4s$ width used as a regulator in Eqs. (29) and (38) of [2] should be replaced with the $2s$ width.

In general, the cascade approximation cannot help to take into account 'real' multi-photon decay modes. The integral cascade width is completely determined by the first decay in the chain and does not involve any information on further subsequent decays. Calculations of such

[2] The value 12 s^{-1} was quoted from Table 1 of [8]. However, this value was computed using the part of the two-photon profile that only includes transitions to virtual intermediate states, which in [8] was defined as 'non-resonant' contribution. In [8] this definition was merely nomenclature, and turned out to be convenient in the computation of the total matrix elements. But as explained in Sect. 4.3 and Sect. 5 of [8] because of interference with the resonant contributions to the total transition matrix element this value *should not* be interpreted as two-photon correction to the $4s \to 1s$ transition rate.

effects within the cascade approximation was one of the purposes of [2].

There are also problems outside of main consideration of [2], which, however, are important for the interpretation of the results. As we can see, the regularization of quantum-mechanical expressions (29) and (38) plays a crucial role in calculations. Paper [2] is devoted to a free hydrogen atom, but it was motivated by study of cosmic recombination of hydrogen, which occurred some 380 000 years after the big bang, when the Universe had cooled to a temperature of about $\sim 3000\,\mathrm{K}$. During cosmological recombination, the atoms existed within an intense bath of the cosmic blackbody radiation. Under these conditions, the cascade chains should not only include *spontaneous decays*, but also *excitations* and *induced decays*, mediated by the cosmic radiation background. This can change the total width of the $3p$ state by $\sim 1\%$ (see [5] for more details). Thus the decay width, used as a regulator, should include effects beyond the free-atom approximation. Notably, in the case of the cosmic recombination the $2s$ and $1s$ states receive a width induced by the blackbody CMB radiation [6].

Next, we have to check whether the width of the initial and final states are important for the consideration. Any partial width should be calculated without introducing the width of the initial state into any denominator of expressions similar to Eqs. (29) and (38) of [2]. Nevertheless, the width of initial state may appear in certain expressions, however for a different reason. It enters through branching ratios (relative probabilities) for the transitions of interest, which needs to deal with combinations such as

$$\frac{W_{3p-2s}}{W_{3p-2s}+W_{3p-1s}} = \frac{W_{3p-2s}}{\Gamma_{3p}}\,.$$

This expression determines the portion of $3p$ states that decay with the emission of three photons (assuming a free decay, where the dominant mode of $2s$ decay is a two photon process). This has to be used in the denominator as total width of the initial state (which in our example is the $3p$ state).

The initial- and final-state widths are even more important in another way. Once we want to consider the dynamics beyond the cascade approximation or wish to derive the cascade approximation from rigorous quantum-mechanical expressions, we have to start with a certain expression similar to Eqs. (29) and (38) of [2]. However, we have to start such an evaluation with 'quasi-stable' initial and final levels. The conditions

$$\frac{\Gamma_{\rm initial}}{\Gamma_{\rm intermediate}} \ll 1$$

and

$$\frac{\Gamma_{\rm final}}{\Gamma_{\rm intermediate}} \ll 1$$

are necessary to validate such an approach.

The cascade approximation means that all the levels are created, propagate and decay in a factorized way. E.g. the lifetime of an 'initial' or 'intermediate' state, and details of their decay do not depend on a way they have been created. Meantime, the expressions such as Eqs. (29) and (38) pretend to go beyond such a factorized description. However, the very formulation of the problem, such as a decay of the $3p$ or $4s$ state, means that we already partly consider a cascade approximation, because the very existence of those states as initial states means that we ignore details of their creation.

As is well-known, off-resonance corrections are larger for broad levels than for narrow ones, and it is reasonable to consider several most narrow levels in a pure resonance approximation. The very consideration of a decay of a certain state into a set of final states within an approach given by Eqs. (29) and (33) of [2] is meaningful only if the initial state together with all possible final states of the decay chains is more narrow than any intermediate state, which means $\Gamma_{\rm init}/\Gamma_{\rm interm} \ll 1$ and $\Gamma_{\rm fin}/\Gamma_{\rm interm} \ll 1$.

For example, if we consider a frequency distribution of emission lines, the line width of a particular resonance photon is determined by the width of both initial and final states. That means that in a chain of transitions we need to take into account both widths, and thus both the states should be treated as metastable (unstable) for the same reason. We cannot really consider any of them as an 'initial' or 'final' state of a cascade chain. We need to introduce creation of the initial state and decay of the final state, unless one of them lives much longer than the other and its width can be neglected.

For the consideration of the $3p-1s$ three-photon decay with a resonance at $2s$ the width of resonance $3p-2s$ photon is determined by the ambiguity in the very formulation of the problem of decay of $3p$ state, while the width of sum of two frequencies of the $2s-1s$ resonance is determined by the $2s$ width. The uncertainty in energy of the initial state is more important than the width of the $2s$ state. That invalidates the very consideration of decay of any state (such as $3p$ or $4s$) into the $1s$ state via the $2s$ state. In principle, such a consideration should consider the $2s$ state as a stable one.

However, if we are to eventually arrive at a pure resonance approximation it is not important in which order we 'break' the chain and which levels we already consider in the cascade approximation. Finally, all accessible intermediate states become resonances. Since paper [2] presumes to derive the results in a pure resonance approximation, the formulation of the problem of the decay of the $3p$ and $4s$ state is not quite correct, but should eventually produce correct results. That is because of the fact that there are two kinds of parameters. One is for the ratio of a width and a characteristic frequency, and the other is ratios of different widths. The latter are important to partially consider dynamics beyond the cascade descriptions. The former are always small by a factor $\alpha(Z\alpha)^2$ or less and they are sufficient to derive the cascade results.

Consideration of any modes beyond the leading contributions, which are with one-photon decays of any initial state to lower states, are meaningless for the integral line width, but may be important for a differential width as explained in [3]. Indeed, there is no real separation between tail of the 'resonance' terms and 'off-resonance modes' and interference terms and for the differential effects one has to deal with a complete width.

This aspect of the problem is also important for recent computations of the cosmological recombination process [5, 7], where deviations of the differential cross-sections from the normal Lorentzian profile [8, 9] are accounted for, in both two-photon decay channels (e.g., $3d \to 2p \to 1s$) and Raman-events (e.g. $2s \to 3p \to 1s$). No explicit separation in cascade or off resonance contributions is made, but the total interaction of atoms with the ambient cosmic radiation background, including photon production, photon absorption, and photon scattering, are taken into account consistently.

The work was supported in part by DFG (under grant # GZ HA 1457/7-1) and RFBR (under grant # 11-02-91343). Discussions with R.A. Sunyaev are gratefully acknowledged.

[1] S. G. Karshenboim, V. G. Ivanov, and J. Chluba, subnitted to Phys. Rev. A.
[2] D. Solovyev and L. Labzowsky, Phys. Rev. A **81**, 062509 (2010).
[3] S. G. Karshenboim and V. G. Ivanov, Astronomy Letters **34**, 289 (2008).
[4] V. G. Ivanov and S. G. Karshenboim, JETP **182**, 656 (1996); Phys. Lett. A **210**, 313 (1996).
[5] J. Chluba and R. M. Thomas, MNRAS, **412**, 748 (2011).
[6] J. Chluba and R. A. Sunyaev, A&A **446**, 39 (2006).
[7] Y. Ali-Haïmoud and C. M. Hirata, Phys. Rev. D **83**, 043513 (2011).
[8] J. Chluba and R. A. Sunyaev, A&A **480**, 629 (2008).
[9] C. M. Hirata, Phys. Rev. D **78**, 023001 (2008)